

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Systematic in-situ XAFS investigation of binary and ternary electrocatalysts in fuel cell operation	Experiment number: ME-846
Beamline: BM29	Date of experiment: from: 16/06/04 to: 21/06/04	Date of report: 30/07/04
Shifts: 12	Local contact(s): O. Mathon	<i>Received at ESRF:</i>
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Report:

Systematic in-situ XAFS investigation of binary and ternary electrocatalysts in fuel cell operation

Aim:

A special in-situ cell has been developed to enable X-ray absorption measurements during fuel cell operation. The main aim of these investigations is to pursue potential- and fuel-dependent structural (EXAFS) and electronic (AXAFS) changes of the anode catalyst. Beamline BM29 is especially suited for these experiments, as it is equipped with an excellent fluorescence detector.

Measurements and improvements compared with last beamtime (ME-608):

Four different membrane electrode assemblies (MEAs) were prepared for the XAS measurements: a) with a carbon-supported Pt-Ru alloy anode catalyst, b) with a mixture of carbon-supported Pt and carbon-supported Ru as anode catalyst, c) with an unsupported Pt-Ru alloy catalyst and d) with a ternary carbon-supported PtRuMo catalyst. All MEAs were operated first with pure hydrogen and in a second series with a H₂/150 ppm CO feed, and spectra were recorded at different potentials at the Pt L₃- and the Ru K-edge. In order to

complement the in-situ measurements one spectrum was taken before and one after operation at elevated temperatures but without gas feed. Approximately 80 spectra were recorded during the beamtime, which will be analysed in detail over the next months.

One main improvement of this beamtime over the previous one is shown in fig. 1. Last year, a strange pre-edge feature appeared in the Pt spectra which could not be explained (black line, see also report ME-608). Moreover, the overall edge height was comparatively small. These drawbacks were greatly enhanced as the cell's Be window was replaced by a thick Kapton[®] foil resulting in a much higher intensity and an improved resolution. It is assumed that a W impurity in the Be window caused the strange pre-edge signal which is no longer present in the new spectra (red line).

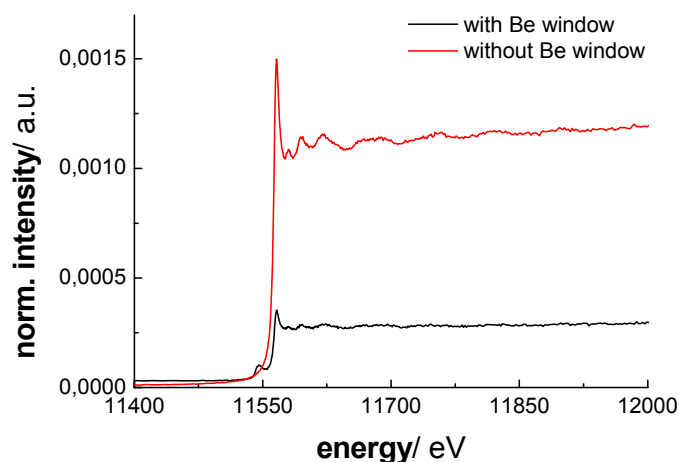


Fig. 1. Comparison of Pt spectra with and without Be window in cell

The optimum set-up for our experiments was found to be the commercial fuel cell hardware with a Kapton[®] foil beam window in fluorescence geometry (fig. 2).

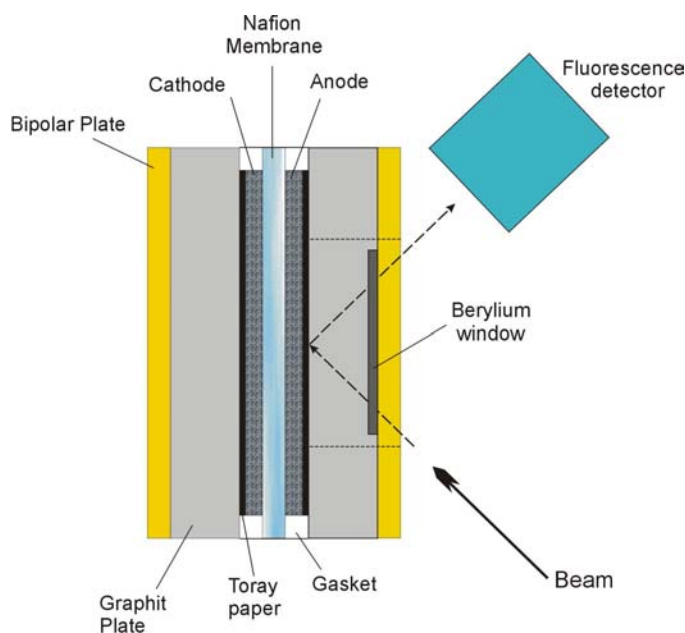


Fig.2. Set-up of the in-situ cell in fluorescence geometry

In Figure 3 some preliminary results at the Ru *K*-edge are presented.

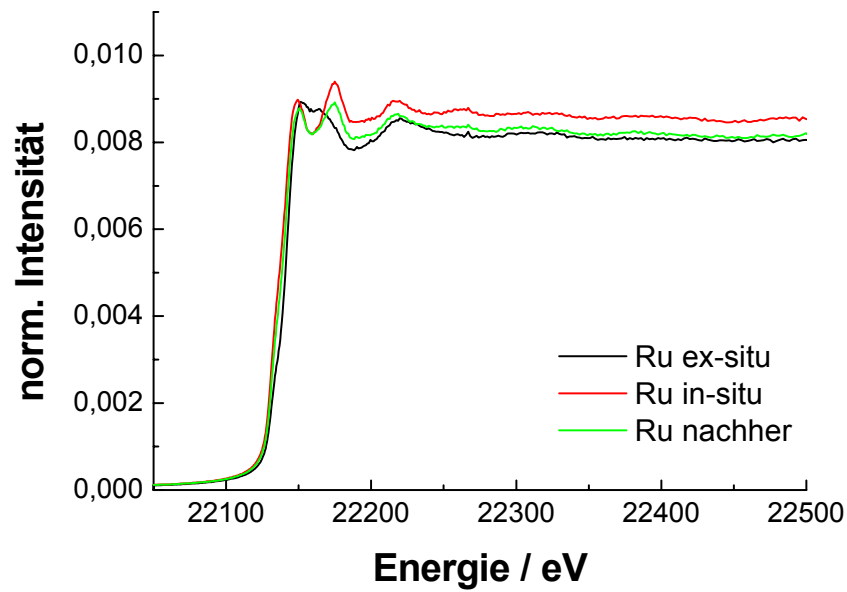


Fig. 3. Ru spectra before, during and after fuel cell operation

Significant differences between the spectrum before operation and the ones during and after operation are revealed. Before operation, most of the ruthenium in the catalyst is oxidized (black line). But after contact with the fuel, ruthenium is completely reduced, and the spectrum resembles one of metallic Ru nanoparticles.

In Figure 4, the fitted Fourier transforms (FT) of Pt before and during hydrogen operation are shown. The preliminary results are summarized in table 1.

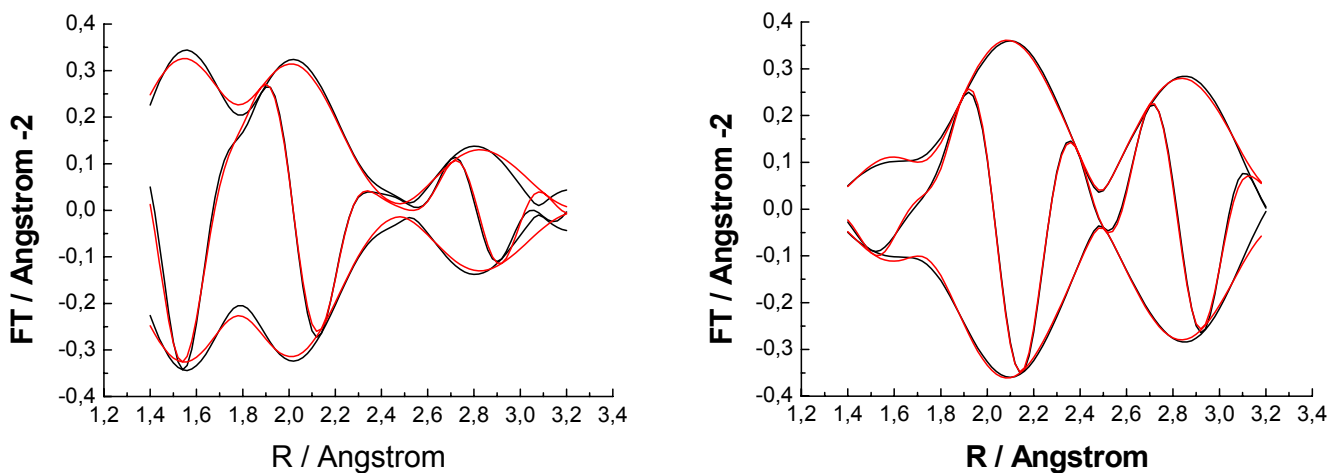


Fig. 4. Fourier transforms of Pt before operation (left) and during operation in hydrogen (right); black line = data, red line = fit

Upon the first contact of the catalyst with the fuel, significant changes take place in the number of Pt-Pt, Pt-Ru and Pt-O nearest neighbours (N values). The findings suggest the (partial) reduction of surface oxides existing on the air oxidized catalyst particles before operation. During operation, further changes in the number of Pt-Pt and Pt-Ru contributions were observed with increasing potential but of much smaller magnitude. Measurements of a supported and an unsupported Pt-Ru alloy catalyst closely resemble each other.

The particle size increases slightly during operation, while the number of Pt-O contributions decreases from $N_{\text{Pt-O}}=1.4$ to 0.3. This is in good agreement with the decreased white-line intensity in operation. Furthermore, the number of Pt-Ru nearest neighbours increases with potential. It is assumed that ruthenium oxides on the particle surfaces become reduced during operation, and ruthenium atoms “move” inside the particles to form a more homogeneous alloy. The as-received catalysts (ex-situ, before operation) show strained Pt-Pt and Pt-Ru distances, possibly associated with the small particle sizes. However, $r_{\text{Pt-Pt}}$ and $r_{\text{Pt-Ru}}$ approach their equilibrium values during operation.

Table 1. Preliminary fit results for three different Pt spectra

	scatterer	N	r	Δs	E0
Pt before	Pt-Pt	3.7	2.68	0.004	9.6
	Pt-Ru	1.7	2.70	0.003	-11.0
	Pt-O	1.4	1.97	0.003	5.9
Pt in-situ	Pt-Pt	4.1	2.73	0.004	3.3
	Pt-Ru	4.1	2.73	0.008*	-8.7
	Pt-O	0.3	1.95	0.010*	5.0
Pt after	Pt-Pt	4.7	2.72	0.003	4.7
	Pt-Ru	2.7	2.71	0.004	-8.7
	Pt-O	0.3	1.99	0.002	5.4

* Δs is higher for the in-situ sample associated with the elevated working temperatures.

Now that the in-situ cell and instrumental method is established, more complex investigations are planned in a future proposal.